I. HYDROGEN BONDING BY C-H
II. HYDROGEN BONDING BY S-H
III. EFFECT OF SUBSTITUTION ON THE DISSOCIATION OF HEXAARYLETHANES: META PHENYL GROUP

BY

EMANUEL GINSBERG

B.S., New York University, 1936

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1940

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I. HYDROGEN BONDING BY C—H

INTRODUCTION

The concept of association through hydrogen bonding proposed by Latimer and Rodebush[1] in 1920 to explain the abnormal properties of certain liquids has been utilized with considerable success in understanding the behavior of liquids and solutions. In particular it has proved useful in explaining and predicting abnormally high solubility of certain organic substances in various types of solvents, the high heats of mixing, abnormal viscosities and other large deviations from the law of "ideal" liquid mixtures.

The present study stems from the need for more information concerning the incidence of and factors influencing hydrogen bonding by C-H.

DISCUSSION OF RESULTS

The heats of mixing a variety of organic liquid pairs one member of which contains a C-H hydrogen capable of forming a hydrogen bond to a donor atom, and the other a donor oxygen or nitrogen have been measured calorimetrically. It has been shown that the major portion of the heat produced on mixing electron pair donor and electron pair acceptor molecules can be accounted for by the assumption of the formation of intermolecular hydrogen bonds between unlike molecules.

By measuring the heat of mixing of a number of donor liquids with the same acceptor liquid a comparison of their donor ability has been made and some facts related to this property established. Observations have been made which indicate that nitromethane, nitriles, ethylal and orthoformic ester are associated through hydrogen bonds.

By using different acceptor molecules with the same donor liquid in the heat of mixing measurements, some of the factors influencing the ability of hydrogen atoms attached to negatively substituted carbon atoms to form intermolecular hydrogen bonds have been established. The following factors have been shown to affect hydrogen bonding: (1) the substituent on the C-H, (2) steric hindrance, (3) unsaturation adjacent to the C-H. Vinylogs of haloforms such as the benzotrihalides exhibit active hydrogens.

A correlation between the results of studies of hydrogen bonding between unlike molecules obtained by the heat of mixing, solubility[2] and infrared[3] methods has been made. The results indicate that, in general, the factors responsible for one are also responsible for the others, particularly in the results obtained with heat of mixing and solubility measurements. This indicates that hydrogen bonding is of major importance in producing high solubility and high heat of mixing.

II. HYDROGEN BONDING BY S-H
THEORETICAL AND DISCUSSION OF RESULTS

Hydrogen bonding involving hydrogen attached to fluorine, oxygen, nitrogen[1,4] and more recently to negatively substituted carbon atoms[2,5] has been shown to occur. These results suggest that hydrogen bonding is more general than hitherto believed and that whenever a hydrogen is attached to another atom by a sufficiently ionic link it will bond to an unshared pair of electrons of a donor atom.

The heat effects on mixing *n*-heptyl and phenyl mercaptans with donor solvents were measured. Heptyl mercaptan gave no heat on mixing with N,N-dimethyl acetamide, ethyl ether, acetone or benzene indicating no intermolecular hydrogen bonding occurred. However, the more acidic phenyl mercaptan gave 572 calories per mole of solution with N.N-dimethyl acetamide, 173 calories with ethyl ether, and 150 calories with acetone. From the magnitude of the heats of mixing alone it appears that S-H←O or N bonds are considerably weaker than C-H←O or N bonds formed by chloroform. The location of the maxima at 0.5 mole fraction suggests the formation of an equimolar complex in each case.

Boiling point and other studies[4,6] indicate that mercaptans are unassociated through hydrogen bonding.

SUMMARY

The heats of mixing of *n*-heptyl and phenyl mercaptans with N,N-dimethyl acetamide, ethyl ether, acetone, and benzene have been measured. The results afford evidence of hydrogen bonding to donor oxygen and nitrogen by phenyl mercaptan, but not by *n*-heptyl mercaptan. The failure of aryl mercaptans to show association is a result of the weak donor ability of the sulfur atom for hydrogen bonding and not from any

lack of acceptor ability on the part of the hydrogen of the S-H link. It is pointed out that whenever a hydrogen is attached to another atom by a sufficiently ionic link, hydrogen bonding is possible.

III. EFFECT OF SUBSTITUTION ON THE DISSOCIATION OF HEXAARYLETHANES: META PHENYL GROUP INTRODUCTION

Resonance of the odd electron of the triarylmethyl produced by dissociation of a hexaarylethane has been proposed[7] to account for the stability of the free-radical thus formed. A comparison of the degree of dissociation of hexaarylethanes which have phenyl groups substituted for hydrogen atoms in the meta and para positions with respect to the ethane carbon atoms is of considerable interest in testing the resonance theory of dissociation of hexaarylethanes.

EXPERIMENTAL AND DISCUSSION OF RESULTS

Meta-bromobiphenyl was prepared by diazotization of *m*-bromoaniline and treatment of the diazonium salt with benzene and alkali according to the method of Gomberg and Bachmann.[8] This bromide was converted into the Grignard reagent and then into tri-*m*-biphenylcarbinol, phenyl-di-*m*-biphenylcarbinol and diphenyl-*m*-biphenylcarbinol by treatment[8] with diethyl carbonate, ethyl benzoate and benzophenone respectively. Only diphenyl-*m*-biphenylcarbinol was obtained in crystalline form, m.p. 104-105°. Tri-*m*-biphenylcarbinol was converted to chloromethane, m.p. 200-201°, by treatment with dry hydrogen chloride.[7] The ethyl ether of diphenyl-*m*-biphenylcarbinol was prepared, m.p. 78-79°, and either it or the carbinol could be converted into chloromethane, which melted at 86-87°, by treatment with acetyl chloride.

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VITA

The writer was born in New York City on July 26, 1915. He attended the public schools of that city and was graduated from De Witt Clinton High School in June, 1932. He entered New York University in the fall of 1932 and received the B.S. degree in June, 1936. In the fall of 1936 he entered the Graduate School of the University of Illinois, received the M.S. degree in June, 1937, and has continued in attendance at this school.